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**SYNTHESIS AND CHARACTERIZATION OF A CHITOSAN DERIVATIVE FOR
ELECTRO-OPTICAL APPLICATIONS**

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Chitin is a naturally occurring polymer of $\alpha(1-4)$ poly N-acetylglucosamine found primarily in the shells of crustaceans and insects. This polymer is chemically and thermally stable and physically durable as a consequence of hydrogen bonding which causes the alignment and ordering of the polymer chains into microcrystals which aggregate into sheets with chiral nematic order. Industry has attempted to take advantage of chitin's properties and low cost (chitin is a waste product of the shellfish industry) to produce durable fibers and other products. This has been largely unsuccessful because of chitin's non reactivity and insolubility.

Chitosan is the deacetylation product of chitin and retains many of the structural properties of chitin (3). Unlike chitin, chitosan is soluble in aqueous solution at reduced pH making it easier to be processed into fibers and films than chitin (4). Chitosan and its derivatives are now used in such commercial applications as wound dressings, waste water treatment, and in pharmaceuticals (5-8).

In this study, we have synthesized a chitosan derivative, N-para-nitrophenyl chitosan (NPNPC), as a model material with potential applications in electro optics.

NPNPC was synthesized by the nucleophilic substitution of the fluorine atom in para-fluoronitro aniline by the amino groups of chitosan in the following manner. 5 grams of chitosan were placed into 100 ml of DMSO. 4 grams of triethylamine, 20 grams of potassium carbonate, and 3 grams of para-fluoronitro aniline were added with stirring. The mixture was refluxed at 50°C with stirring for 4 days. The chitosan never dissolved in this mixture but swelled and eventually changed from a white to a yellow color. The polymer was recovered by filtration, washed with ethanol, dried in a vacuum dessicator and weighed. The reaction was estimated to be 80 - 90% complete based on the increase in the mass of the polymer. The solubility of the polymer is reduced when compared to chitosan as would be expected since the secondary amine generated is more difficult to protonate than the original primary amine. The polymer is not soluble (2% by weight) in 2% acetic or 2% formic acid but is soluble in 5% formic acid (1% by weight). The solution is very viscous but sonifying the sample for 30-60 seconds reversibly reduces the viscosity. NMR spectroscopy of NPNPC revealed the expected peaks for the desired product although the high viscosity of the material broadened the peaks.

Samples used for film preparation were washed repeatedly with acetone and baked dry. 1.5 ml samples of 1% NPNPC in 5% formic acid were sonified for 30 to 60 seconds and centrifuged at room temperature (10,000RPM in a microfuge) for 10 minutes to remove any debris or undissolved polymer. Films were produced by on slides coated with oriented teflon by spin coating or allowing the sample to dry without spinning. Films on quartz discs were formed by drying 50 microliters of sample with and without shearing.

The films were examined by light microscopy through crossed polars to detect areas in which ordering had occurred. Films formed on teflon coated glass slides with and without spinning showed regions where the polymers aligned as well as large amorphous regions. Small regions displaying chiral nematic ordering were also observed. Films formed on quartz discs without shearing displayed no ordering while films formed with shearing contained a number of different ordered domains including amorphous polarizing domains, chiral nematic domains, and linearly aligned domains.

Plans for continuing this work include optimizing the formation of ordered films, comparing the NLO properties of both ordered and amorphous films, and the synthesis of other substituted chitosans.

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